COATING COMPOSITIONS COMPRISING BUSOXINONE

The present invention concerns coating compositions comprising busoxinone which protect surfaces or objects in frequent or constant contact with water for a long period of time from settlement by aquatic organisms, also known as fouling.

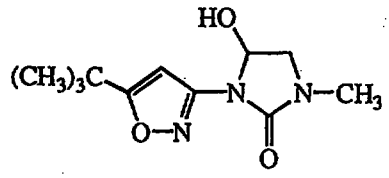
Surfaces or objects exposed to humid or aqueous environments are readily colonized by aquatic organisms such as algae, fungi, bacteria, microbes, and aquatic animals such as, e.g. tunicates, hydroids, bivalves, bryozoans, polychaete worms, sponges, barnacles, molluscs and crustacea. As these organisms settle on or attach to said surfaces, the value of the exposed objects diminishes. The attachment or settlement of said organisms is also known as 'fouling' of a structure. The exterior, but possibly also the interior of the object may deteriorate, the surface changes, e.g. from smooth, clean and streamlined to rough, foul and turbulent, the weight of the object increases by the deposit of the organisms and their remnants, and the vicinity of the object may become obstructed or encumbered. The function of the object and system involved lowers and the quality of the aqueous environment deteriorates. The common method of controlling the attachment of fouling organisms is by treating the structure to be protected with a coating which comprises an antifouling agent.

For many years, coating compositions comprising organotin compounds have been used, mainly because of their excellent antifouling properties. However, the negative influence of the highly toxic organotin compounds on the environment and accumulation of such toxic compounds in organisms has been pointed out as problematic. A notice for restricting their use has been issued by the Ministry of Transportation of Japan. Therefore, it is worthwhile to develop alternative antifouling coating compositions as substitutes.

A major factor in determining the effectiveness of an antifouling coating composition is the release rate of the antifouling agent out of the coating into the aquatic environment. If the antifouling agent is released too rapidly, it will be exhausted quickly and the coating will have to be re-applied to the surface to be protected, thereby shorthening the interval between normal service periods. Said re-appliance of the antifouling coating is costly and time-consuming.

Fouling of surfaces or objects exposed to humid or aqueous environments often starts with the attachment or settlement of algae. This roughens the smooth surface thereby easing the settlement of other fouling organisms such as, e.g. tunicates, barnacles, crustacea, molluscs and the like. Hence, the algicidal properties of coatings which protect surfaces from fouling are of primary interest.

(±)-3-[5-(1,1-Dimethylethyl-3-isoxazolyl]-4-hydroxy-1-methyl-2-imidazolidinone, also known as busoxinone or PPG 1259, was first disclosed in US-4,268,679, as a herbicide.



busoxinone

EP-0,044,185, published on 20 January 1982, and US-4,421,546 disclose busoxinone as a herbicide effective for pre- or post-emergence control of ground weeds and aquatic weeds, including algae. Said art documents also disclose aqueous sprays, drenches, solid powders or invert emulsions comprising busoxinone. Further, EP-0,127,433, published on 5 December 1984, encompasses synergistic compositions comprising fluridone and busoxinone, useful as algicides and aquatic herbicides.

The pre- and post-emergence herbicidal activity of busoxinone is further described by W. Bond in Test Agrochem. Cultiv., 8, p. 106-107, 1987 (CAN 107:54066) and A.K. Wilson et al. in abstract no. 859,090 Gov. Rep. Announce Index U.S., 88(23) 1988, (CAN 111:35070).

Said prior-art documents, especially EP-0,044,185 and US-4,421,546, disclose formulations of busoxinone, used to control or eliminate the growth of aquatic plants, which are either directly applied onto said aquatic plants, or dispersed into the aqueous environment containing the submerged or floating aquatic plants. The present invention differs from said art documents in that it provides for coating compositions comprising busoxinone.

Unexpectedly, it was found that despite the high solubility of busoxinone in water, the release rate or bleeding velocity of busoxinone out of the coating compositions into the aqueous environment is sufficiently low to provide coatings having excellent antifouling properties for a long period of time.

Hence, the present invention provides for coating compositions comprising an effective algicidal amount of busoxinone which inhibit the attachment or settlement of algae to surfaces in a humid or aqueous environment. Said coating compositions are capable of forming coatings having excellent antifouling performance and capable of providing such excellent performance for a period of time long enough to bridge the interval between normal service periods.

The coating compositions of the present invention provide a safer and ecologically more acceptable alternative for current coatings comprising antifouling products based on heavy metals such as cuprous oxide and the like, or those based on organometallic derivatives such as organo-tin compounds. The toxicity of busoxinone to mammals is acceptable and as such it is less hazardous for humans when it reaches the human body by direct physical contact (e.g. during handling or application) or via the food chain. Its bio-degradability ensures that it is less persistent in the environment and that it causes less and shorter environmental pollution and stress. The chemical stability of busoxinone furthermore implies that it is compatible with most non-living materials as such and does not need special precautions such as the addition of agents for stabilizing busoxinone.

The term "fouling organisms" is meant to comprise organisms that attach, settle, grow on or adhere to various kinds of surfaces, in particular in humid or aqueous environments such as, marine waters, fresh waters, brackish waters, rain water, and also cooling water, drainage water, waste water and sewage. Fouling organisms are Algae such as, for example, Microalgae, e.g. *Amphora, Achnanthes, Navicula, Amphiprora, Melosira, Cocconeis, Chlamydomonas, Chlorella, Ulothrix, Anabaena, Phaeodactylum, Porphyridium;* Macroalgae, e.g. *Enteromorpha, Cladophora, Ectocarpus, Acrochaetium, Ceramium, Polysiphonia* and *Hormidium sp.*; fungi; microbes; tunicates, including members of the class Ascidiacea such as *Ciona intestinalis, Diplosoma listerianium,* and *Botryllus schlosseri*; members of the class Hydrozoa, including *Clava squamata, Hydractinia echinata, Obelia geniculata* and *Tubularia larynx*; bivalves, including *Mytilus edulis, Crassostrea virginica, Ostrea edulis, Ostrea chilensia,* and *Lasaea rubra*; bryozoans, including *Electra pilosa, Bugula neritina,* and *Bowerbankia gracilis*; polychaete worms, including *Hydroides norvegica*; sponges; and members of the class Crustacea, including *Artemia*, and Cirripedia (barnacles), such as *Balanus amphitrite, Lepas anatifera, Balanus balanus, Balanus balanoides, Balanus hameri, Balanus crenatus, Balanus improvisus, Balanus galeatus,* and *Balanus eburneus*; and *Elminius modestus*, and *Verruca.*

The coating compositions of the present invention comprise an effective algicidal amount of busoxinone; and polymers or copolymers derived from such monomers as dialkyl siloxanes, (meth)acrylic acid, (meth)acrylic acid esters, vinyl and allyl alcohols and derived esters, maleic acid, styrene, vinylchloride, butadiene, acrylamide, acrylonitrile, or resins such as alkyd resins, polyurethanes, epoxy resins, phenolic resins and urea-formaldehyde resins; and mixtures thereof.

The coating compositions of the present invention can further comprise one or more additives selected from the group consisting of water-repelling agents; surface slipping agents; diluents; organic binding agents; insecticides; fungicides; bactericides; auxiliary solvents; processing additives; fixatives; thickening agents; plasticizers; UV-stabilizers; stabilisers against heat or light; dyes; color pigments; siccatives; corrosion inhibitors; antisettling agents; anti-skinning agents; and antifoaming agents.

Useful additives in said compositions comprise water-repelling agents and surface slipping agents that are capable of imparting a low surface tension of the coating film formed by the polymer or copolymer in the coating compositions.

Busoxinone can be added in neat form to the coating composition or dissolved or suspended in a sufficient amount of diluent. Preferably the diluent consists of one or more of the solvents as they occur in the final composition. Diluents used for the production of the coating compositions should preferably not be readily flammable and should be as far as possible non-toxic to nontarget animals or plants and humans in the relevant surrounding. Diluents suitable for this purpose are, for example, water or, organic solvents such as, for example, aromatic hydrocarbons, e.g. methylbenzene, dimethylbenzene mixtures, substituted naphthalenes; alcohols and glycols and their ethers and esters, e.g. ethanol, ethylene glycol, ethylene glycol monomethyl or mono-ethyl ether; ketones e.g. 2-propanone, cyclohexanone and the like; strongly polar solvents; e.g. *N*-methyl-2-pyrrolidone, dimethyl sulfoxide or dimethylformamide; vegetable oils or epoxidised vegetable oils such as epoxidised coconut oil or soybean oil, and mixtures thereof. Coating compositions can be prepared in the usual way, if necessary, with assistance of solution promotors. Other coating compositions which can be used consist of emulsions, dispersions or suspensions of busoxinone in water or suitable diluents, or also concentrates for preparing such emulsions, dispersions or suspensions which can be directly adjusted to the required concentration. For this purpose, busoxinone is, for example, mixed with a dispersing, suspending or emulsifying

agent. Busoxinone can also be dissolved or dispersed in a suitable inert solvent and mixed simultaneously or subsequently with a dispersing or emulsifying agent.

The coating compositions of the present invention may further comprise other adjuvants conventionally employed in the art of formulation. These depend on specific applications and the user's preference. Such adjuvants are, for example, organic binding agents (e.g. chemically drying organic binder-forming polymers such as alkyd resins or physically drying organic binder-forming solids by solvent evaporation); insecticides such as, for example, chlorinated hydrocarbons, e.g. endosulfan, organophosphates, e.g. chloropyriphos, pyrethroids, e.g. permethrin and the like; additional fungicides and bactericides such as alcohols, e.g. ethanol, 2,3,3-triiodallyl alcohol; aldehydes, e.g. formaldehyde, glutaraldehyde; formaldehyde releasing compounds, e.g. 2-bromo-2-nitro-propane-1,3-diol (bronopol), 2-bromo-2-nitropropan-1-ol; reaction products of amines and formaldehyde, e. g. triazines, 3,5-dimethyltetrahydro-1,3,5-2*H*-thiadiazine-2-thione; reaction products of amides and formaldehyde, e.g. 1-hydroxymethyl-2-thiono-1:2-dihydro-benzothiazol-*N*-hydroxymethyl-benzothiazolinthione; phenols, e.g. 2-phenylphenol, pentachlorophenol; organic acids, e.g. propionic acid, benzoic acid, salicylic acid, naphthenic acid copper salts; inorganic acids, e.g. boric acid; amides, e.g. 2,5-dimethyl-*N*-cyclohexyl-*N*-methoxy-furan-3-carbonamide; carbamates, e.g. 3-iodopropargyl-*N*-butylcarbamate (IPBC), methyl-*N*-benzimidazol-2-ylcarbamate (Carbendazim), methyl-*N*-(1butylcarbamoyl)-benzimidazol-2-ylcarbamate (benomyl), zinc dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate, bis-(dimethylthio-carbamoyl)disulphide; pyridine derivatives, e.g. 2-mercapto-pyridine-*N*-oxide, 2-chloro-6-(trichloromethyl)pyridine, 2,3,5,6-tetrachloro-4-(methylsulphonyl)pyridine, copper 8-hydroxyquinoline, 1-ethyl1,4-dihydro-7-methyl-4-oxo-1,8-naphthyridine-3-carboxylic acid; azoles, e.g. tebuconazole, propiconazole, azaconazole, imazalil; heterocyclic compounds, e.g. 2-methyl-3(2*H*-isothiazolone, 5-chloro-2-methyl-3(2*H*)-isothiazolone, 2-n-octyl-4-isothiazolin-3-one, 4,5-dichloro-2-(n-octyl)-4-isothiazolin-3-one, 1,2-benzisothiazolin3-one, 2-methyl-4,5-trimethylene-4-isothiazolin-3-one, 2-(4-thiazolyl)-benzimidazole, 2-mercaptobenzothiazole, 2-(thiocyanomethylthio)benzthiazole; *N*-haloalkylthio compounds, e.g. *N*-trichloro-methylthiophthalimide, folpet, *N*-trichloromethylthio-4-cyclohexane-1,2-dicar-boximide, captan, *N*-1,1,2,2-tetrachloroethylthio-4-cyclohexene-1,2-dicarboximide, captafol, dichlofluanide, tolylfluanide; compounds with activated halogen groups, e.g. chlorothalonil; surface active agents, e.g. guanidines and biguanides; various compounds, e.g. pimaricine, tridemorph, methylene bisthiocyanate, tolyl sulfone, dicyanobutane; active natural products, e.g. streptomycin; auxiliary solvents such as

ethylglycol acetate and methoxypropylacetate; processing additives; fixatives such as carboxymethyl-cellulose, polyvinyl alcohol, paraffin; thickening agents; plasticizers such as benzoic acid esters and phthalates, e.g. dibutyl phthalate, dioctyl phthalate, didodecyl phthalate; UV-stabilizers; stabilisers against heat or light; dyes; color pigments; siccatives such as cobalt octoate, lead octoate and cobalt naphthenate; corrosion inhibitors; antisettling agents; anti-skinning agents such as methyl ethyl ketoxime; antifoaming agents and the like. Generally, the adjuvants are not essential to the practice of the present invention but are included in particular formulations, especially in coating formulations to optimize overall effectiveness and ease of application. They can be used therein in the conventional amounts.

The coating compositions of the present invention can comprise further components known for use in coatings, for example plasticisers, thickening and anti-settling agents, auxiliary film-forming resins and stabilisers against heat or light. Appropriate formulations are formulated following art-known procedures such as, e.g. busoxinone can be mixed with an extender, which consists of a liquid, semi-solid or solid carrier, and optionally surface-active agents such as emulsifiers and/or dispersing agents.

Coatings formed by the present coating compositions can comprise any number of forms, including paints, gelcoats, varnishes, and the like.

The coating compositions can comprise from 1 up to 75%, in particular from 10 to 50% of busoxinone by weight based on the total weight of the dry mass of said composition (*i.e.* up to 50%, in particular from 5 to 25% of busoxinone by weight based on the total weight of the coating composition). The term "dry mass" represents the total solid content of said coating compositions.

The coating compositions of the present invention are prepared by intimately mixing an effective algicidal amount of busoxinone with the other ingredients such as, polymers or copolymers, resins, and other optional additives such as, water-repelling agents; surface slipping agents; diluents; organic binding agents; insecticides; fungicides; bactericides; auxiliary solvents; processing additives; fixatives; thickening agents; plasticizers; UV-stabilizers; stabilisers against heat or light; dyes; color pigments; siccatives; corrosion inhibitors; antisettling agents; anti-skinning agents; and antifoaming agents.

The coating compositions of the present invention are especially suitable to protect surfaces or objects in constant or frequent contact with water from fouling or attachment or settlement of algae, by applying to said surfaces or objects a coating

composition comprising busoxinone. Examples of said surfaces or objects are for instance, shiphulls; recreational equipment, such as surfboards, jet skis, and water skis; harbor installations; piers and pilings; drying docks; sluice-gates; locks; mooring masts; buoys; offshore oil rigging equipment; drilling platforms; bridges; pipelines; fishing nets; cables and any other object in constant or frequent contact with water

Further, coating compositions in accordance with the invention can be used to protect constructions such as, e.g. swimming pools, baths, cooling water circulation circuits and industrial baths in various installations, e.g. in manufacturing plants or in air-conditioning installations, the function of which can be impaired by the presence and/or the multiplication of algae. Further examples are buildings and parts of buildings such as floors, outer and inner walls or ceilings, or places suffering from dampness such as cellars, bathrooms, kitchens, washing houses and the like, and which are hot-beds for fouling. Fouling not only is problematic from the viewpoint of hygiene and aesthetics, but also causes economic losses because said buildings and/or decorating materials deteriorate more rapidly than desired.

Hence, the present invention also provides the use of coating compositions in accordance with the invention to protect surfaces or objects in frequent or constant contact with water from fouling or from attachment or settlement by algae.

The present invention further provides a method of protecting a surface which comprises applying to the surface a coating composition in accordance with the invention. An especially important use of the method of the invention comprises a method for inhibiting fouling of a ship's hull, which comprises applying to the hull a coating composition in accordance with the invention.

The method also comprises applying busoxinone comprising coating compositions, optionally in an appropriate formulation, to non-living materials by any of the techniques known in the art such as, for example, brushing, spraying, atomising, dipping, soaking, immersing, scattering and pouring.

The following examples are intended illustrate the scope of the invention.

A. Biological Examples

The algicidal properties of busoxinone were compared with those of diuron, which is the generic name for *N'*-(3,4-dichlorophenyl)-*N,N*-dimethyl-urea, a well known algicide.

Example 1 : Bleeding test from coating film

The solubility of busoxinone in water at 25°C is 656 mg/l and the solubility of diuron in water at 25°C is 42 mg/l.

The test compounds, busoxinone and diuron, were added to the solvent-based alkyd coating composition of composition example B.1, and mixed at a concentration ranging from 0.2% to 0.5%. Filter paper strips (4 cm x 4 cm) were treated with said coating compositions comprising either busoxinone or diuron and dried. The filter paper strips were immersed in water (70 ml) at 60°C for 24 hours. The concentration of the test compounds released out of the coating in the water solution was measured by a HPLC method.

Table 1 :

Test compounds	Test concentration (%)	Results (ppm)
busoxinone	0.2	11.0
	0.3	18.9
	0.4	26.4
	0.5	34.2
diuron	0.3	124.9

As illustrated in table 1, despite the higher water solubility of busoxinone compared to diuron, about 10 times less busoxinone bleeds out of the coating into the water solution compared to diuron.

Example 2 : long term efficacy of busoxinone comprising coating composition

a) Filter paper test strips (4 cm x 4 cm) were painted on both sides with a coating composition of example 1 comprising 0.3 % of either busoxinone or diuron. The filter paper strips were dried and weathered by placing said paper strips in water of 50°C for 1 or 5 days.

After the weathering stage, the filter paper strips were placed in an algae culture (*Anabaena sp.*, *Hormidium sp.* and *Chlorella vulgaris*) during 28 days at 25°C.

Test results are summarized in table 2.

Table 2 : deposition of algae after 28 days exposure

	1 day weathering	5 days weathering
control	+	+++
busoxinone	-	-
diuron	-	+

+++: thick deposition observed + : slight deposition observed
++ : fair deposition observed - : no deposition observed

As illustrated in table 2, no deposition of algae occurred on the busoxinone comprising coating after 28 days exposure, despite the higher water solubility of busoxinone when compared to diuron.

b) Filter paper test strips (4 cm x 4 cm) were painted on both sides with the solvent-based acryl silicon coating composition of composition example B.2, further comprising either busoxinone or diuron. The filter paper strips were dried and weathered in water of 50°C for 14 days.
After the weathering stage, the filter paper strips were placed in an algae culture (*Anabaena sp.*, *Hormidium sp.* and *Chlorella vulgaris*) at 25°C. Deposition of algae was measured weekly and summarized in table 3.

Table 3 : deposition of algae

	Concentration (%)	7 days	14 days	21 days	28 days
control	0	+	+	+++	+++
busoxinone	0.3	-	-	+	+
	0.5	-	-	+	+
	0.7	-	-	-	-
diuron	0.3	+	+	+++	+++
	0.5	+	+	+++	+++
	0.7	+	+	+++	+++

+++ : thick deposition observed + : slight deposition observed
++ : fair deposition observed - : no deposition observed

As illustrated in table 3, none or only slight deposition of algae occurred on the busoxinone comprising coating after 28 days exposure, despite the higher water solubility of busoxinone and 14 days weathering at 50°C.

B. Composition examples

Suitable coating compositions are exemplified in composition examples B.1 to B.4. To these compositions an effective algicidal amount of busoxinone is added. Said amount

of busoxinone can range from 0.1 to 50% by weight, based on the total weight of the coating composition (including solvents).

B.1. Polyurethane Resine Enamels and Varnishes (all percentages are by weight)

Titanium Dioxide	22.50
Precipitated Barium Sulphate	3.80
Castor oil-Phthalic acid Resin	45.00
Antiprecipitating Agent	0.08
Toluene	2.60
Butyl acetate	1.00
Additive	0.08
Polyisocyanate	11.25
Toluene	10.00
Butyl acetate	3.69

B.2. Acrylic Urethane Resin Enamels and Varnishes (all percentages are by weight)

Titanium Dioxide	17.600
Precipitated Barium Sulphate	2.400
Poly-Acrylic Resin Varnishes	52.000
Antiprecipitating Agent	0.800
Dispersing Agent	0.160
Toluene	2.000
Xylene	2.000
Butyl acetate	3.037
Silicone Oil	0.003
Polyisocyanate	13.400
Ethyl acetate	6.600

B.3. Poly Vinyl acetate Emulsion Paint (all percentages are by weight)

Poly Vinyl acetate clear	85.0
Titanium Dioxide	15.0

B.4. Poly Acrylic Styrene Emulsion Paint (all percentages are by weight)

Titanium Dioxide paste	33.884
Poly Acrylic Styrene Emulsion	50.452
Texanol	3.542
Thickener Water solution	3.492
Antifoaming Agent	0.208
Water	8.422

Claims

1. A coating composition comprising
(a) an effective algicidal amount of busoxinone, and
(b) polymers or copolymers derived from such monomers as dialkyl siloxanes, (meth)acrylic acid, (meth)acrylic acid esters, vinyl and allyl alcohols and derived esters, maleic acid, styrene, vinylchloride, butadiene, acrylamide, acrylonitrile, or resins such as alkyd resins, polyurethanes, epoxy resins, phenolic resins and urea-formaldehyde resins; and mixtures thereof.

2. A coating composition according to claim 1 further comprising one or more additives selected from the group consisting of water-repelling agents; surface slipping agents; diluents; organic binding agents; insecticides; fungicides; bactericides; auxiliary solvents; processing additives; fixatives; thickening agents; plasticizers; UV-stabilizers; stabilisers against heat or light; dyes; color pigments; siccatives; corrosion inhibitors; antisettling agents; anti-skinning agents; and antifoaming agents.

3. A coating composition according to any of claims 1 to 2 comprising from 1% up to 75% by weight of busoxinone based on the total weight of the dry mass of said coating composition.

4. A process of preparing a coating composition of any of claims 1 to 3 wherein an effective algicidal amount of busoxinone is intimately mixed with the other ingredients.

5. Use of a coating composition according to any of claims 1 to 3 to protect surfaces or objects in frequent or constant contact with water from fouling.

6. Use of a coating composition according to any of claims 1 to 3 to protect surfaces or objects in frequent or constant contact with water from attachment or settlement by algae.

7. A method of protecting surfaces or objects which comprises applying to the surface or object a coating composition as defined in any of claims 1 to 3.